Supporting information for

Dual Electrolyte Additives to Achieve High-Rate Cycle Performance of Lithium-Ion Batteries with a High Nickel Cathode

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1. Experimental Section

1.1 Electrolyte Preparation

No further purification was required for all samples. The electrolyte additives 1 wt.%TMSP (product no. T833843) and 1 wt.% ADN (product no. H814585, Shanghai Macklin Biochemical Technology Co., Ltd.) were added to the conventional electrolyte 1.2 M LiPF6 in EC/DEC/EMC/FEC (3:3:3:1 vol%) (product no. KLD-LP372, Guangdong Canrd New Energy Technology Co. T833843). The electrolyte preparation process was maintained in a glove box under argon atmosphere.

1.2 Cathode preparation

LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode powder (Ningbo Ronbay New Energy Technology Co., Ltd.) was mixed with polyvinylidene fluoride and Super P in N-methyl-pyrrolidone solution at a weight ratio of 8:1:1. The slurry dropped on the aluminum foil was spread evenly using a spatula and vacuum dried at 120°C for 12 hours. Then, the cathodes were finally cut into 12 mm diameter discs for assembling standard CR2032 coin-type cells.

1.3 Electrochemical Measurement

A standard CR2032 button-type asymmetric cell was assembled using the previously prepared 12mm diameter cathode, celgard diaphragm, 16mm diameter lithium metal anode, and 30uL electrolyte on each diaphragm side. Another Li-Li symmetric cell was prepared using a 16mm diameter lithium metal anode. All standard CR2032 coin-type cells were assembled in the argon-filled glove box with less than 0.01 ppm oxygen and water contents. All electrochemical performance tests were performed on a multi-channel NEWARE battery test system at 30°C. Electrochemical impedance spectroscopy was performed on the AUTOLAB electrochemical station (Metrohm AUTOLAB PGSTAT204) in the 10⁶- 10^{-1} Hz frequency range.

1.4 Material Characterization

Raman spectra were characterized by the Laser Raman Spectrometer HORIBA. The XPS spectra were acquired utilizing an Al K-alpha X-ray source (1486.6 eV) and dual-beam charge neutralization on a Thermo Fisher ESCALAB Xi+ X-ray photoelectron spectrometer. Gemini SEM 500 Field-Emission Scanning Electron Microscope (FESEM) was used to analyze the morphology of the anodic particles on the surface of the electrode after 50 cycles at an accelerating voltage of 2 kV.

2. Density functional theory calculation

We employed the density functional theory $(DFT)^{1-3}$ and $DFT + U^{4-6}$ method, implemented in the VASP program package⁷, to carry out our computational work. Hubbard parameters used U_{eff} for 3d states of Ni and the value of U_{eff} was calculated by the linear response approach⁸. The calculated U_{eff} parameters are 6.7 eV which is correspond will with former research^{5,9-10}. During the calculations, the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)^{11,12} was utilized in combination with the projector augmented wave (PAW)^{13,14} pseudopotentials. The van der Waals correction was taken into account by using the DFT-D3 method with Becke-Johnson damping function¹⁵. To obtain the fully relaxed structure of LiNiO₂ slab, 500 eV was set as the kinetic energy cutoff for the plane-wave basis, which has been tested for the convergence of the total energy. Gamma only k-point was used to sample the Brillouin zone. To ensure the accuracy of the calculations, an energy threshold of 10⁻⁶ eV and a force threshold of 10⁻² eV/Å were used. A vacuum region with a width of 30 Å was implemented to avoid the effects of vertical periodicity-induced interactions. For the calculation of solvent molecules, the size of the periodic models has dimensions of 20×20×20 Å³. To eliminate the local effect of transition metal configurations on the reactivity of solvent molecules, the LiNiO₂ slab is constructed to simplify Ni-rich NCM811. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of solvent molecules were calculated after structure optimization. The overall adsorption energy (ΔE) was calculated as: $\Delta E = E_{ads}$ $-(E_{sol}+E_{slab})$, where E_{ads} is the total energy of the optimized structure of each solvent adsorbed on the

LNO slab, E_{sol} and E_{slab} are the energy of the independent solvent molecule and the clean LNO slab, respectively. The pictures of structures were produced by VESTA¹⁶. REFERENCES

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